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HEAT OF ADSORPTION OF OXYGEN ON TUNGSTEN
by

W. E. Grummitt, B.Sc.

University of Alberta

April 1941.

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A THESIS

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April 19, 1941.



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HEAT OF ADSORPTION OF OXYGEN ON TUNGSTEN

Submitted in Partial Fulfillment
of the
Requirements for the Degree of
Master of Science

by

W. E. Grummitt, B.Sc.

Under the Direction of

Dr. J. L. Morrison

Time Devoted to this Work - 7 Months

Edmonton, Alberta.

April, 1941.

The author wishes to express his appreciation to all who have assisted in the completion of this work:

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HISTORICAL INTRODUCTION - GENERAL.

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For a considerable time it has been known that porous substances like wood charcoal can take up large quantities of gas. Scheele, in 1777, observed that vapors brought into contact with charcoal at low temperatures in some way combined with it, but these vapors could be recovered by the application of heat. Gas so taken up is said to be adsorbed and the charcoal or other substance is called the adsorbent.

Although numerous observations of a similar nature were made by other workers, the subject received little serious consideration until nearly 50 years later.

The phenomenon of adsorption of gases by solids received considerable attention in connection with catalysis. Faraday (15), in 1833, described experiments on the reaction of hydrogen and oxygen at the surface of platinum. He believed that molecules of the gases, being condensed on the surface, were in far closer proximity to one another, and so in a more favorable condition for the reaction to occur.

As a result of this and similar experiments a systematic study of the phenomena related to catalysis was begun, in which adsorption was considered to be of fundamental importance.

Also related to adsorption is the production of electric lamps with filaments which will have considerable life. This

often requires that the residual gas be removed. Many researches on this problem have been undertaken, particularly by Langmuir for the General Electric Company. The object of those researches was to remove the adsorbed layers of gas from the glass walls and metal surfaces, also to produce a final vacuum by removing the last traces of gas by adsorption on suitable surfaces.

At liquid air temperatures, the adsorption of gases by wood charcoal is almost complete. Dewar used this phenomenon to produce a very high vacuum by placing charcoal, cooled to the temperature of liquid air, in an already partially evacuated space.

At higher temperatures, however, a definite equilibrium is set up between the adsorbed substance and the gas. It is found that for a given mass of gas at a given temperature, the mass of adsorbed gas is proportional to the pressure. This is usually expressed in the form of an isotherm, a relationship between pressure and amount adsorbed at constant temperature.

The early theories of adsorption assumed that the layer of adsorbed gas was of considerable thickness, becoming gradually less dense with increasing distance from the surface. There were, however, serious errors possible in the measurements on which such theories were based.

Most of the original experiments were carried out with porous materials such as charcoal. The nature of these adsorbents

made it impossible to determine the area of the effective adsorbing surface. In determinations where metal foils and similar adsorbents of known surface area were employed, layers were closely packed in order to obtain a sufficiently large adsorbing surface. As a result, enormous numbers of capillary spaces were formed. The saturated vapors and high pressures used then brought about condensation to the liquid state in these capillaries. Another serious error consisted in the use of substances which actually dissolved the gas thought to be only adsorbed.

As a result of experiments where the above difficulties were eliminated, Langmuir (5) proposed the theory that the adsorbed film generally is not more than one molecule in thickness. This theory indicated a sharp boundary between the adsorbed layer and the gas phase. It is supposed that when a molecule impinges on any solid or liquid surface, it does not rebound elastically, but condenses on the surface, being held by the field of force of the surface atoms. Some of these molecules may subsequently evaporate from the surface. Thus adsorption is considered to be a balance between evaporation and condensation processes, the amount of gas adsorbed depending upon the time interval between these processes.

Langmuir (4) first worked with freshly cleaved mica surfaces, and later with drawn metal filaments. He found that

properly drawn tungsten wires have a real surface area very close to the apparent surface area. This property makes such a wire a very desirable material as an adsorbent.

Roberts (2) has developed a technique through which the nature of the adsorbed films on tungsten can be elucidated. It consists of determining the change in the accommodation coefficient during the process of adsorption. Roberts and coworkers have studied heats of adsorption, isotherms, rates of adsorption and the kinetics of formation of adsorbed gases on tungsten (14,9,16). Their observations indicated that there are at least two films of oxygen on tungsten. Referring to the paper of Morrison and Roberts (9), the first film is shown to be composite and complete at all pressures. Most of it is stable up to a temperature of 1700°K ; the remainder of this film becomes unstable at from 900° to 1100°K . This composite film is directly in contact with tungsten. On top of it is adsorbed another film, presumably molecular oxygen.

The amount of heat evolved when a gas adsorbs on a solid surface, called the heat of adsorption, indicates the nature of the forces holding the gas particle to the solid surface. In the case of oxygen on tungsten, Roberts (14) found the heat of adsorption of the more stable part of the first film to be about 135,000 calories per gram molecule of oxygen, and of

the less stable part, about 50,000 calories. This indicates that the binding between oxygen and tungsten in the more stable part of the film is chemical in nature, that is, similar to that between two atoms in a stable molecule. Also, the forces holding the less stable part to tungsten are considerable.

It is the purpose of this thesis to present measurements of the heat of adsorption of the second, molecular oxygen film. This film is not directly attached to tungsten, but rather to oxygen already adsorbed on tungsten.

INTRODUCTION TO HEAT OF ADSORPTION MEASUREMENTS.

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Suppose a gas is admitted to an adsorbent in successive small quantities, so that the amount adsorbed increases by $A_1, A_2, A_3 \dots$; the corresponding quantities of heat evolved will be $Q_1, Q_2 \dots$. The integral heat of adsorption for a concentration A is the limiting value of Q when the increments are indefinitely small. The differential heat of adsorption is the limiting value of dQ/dA when dA is indefinitely small.

Measurements of heats of adsorption by the method indicated above are usually termed direct measurements. A known quantity of gas is admitted to the adsorbent contained in a calorimeter, and the heat produced is measured by the temperature rise.

Krulyt and Modderman (2) have reviewed all available data on heats of adsorption prior to 1930. Charcoal and silica gel form the adsorbent in most of the determinations and the measurements are direct, the adsorbent being contained in the calorimeter. It is, however, possible to use the adsorbent itself as a calorimeter.

Roberts (14) determined the heat of adsorption of hydrogen on tungsten, also the first layer of oxygen on tungsten. In these measurements, a tungsten filament was used both as a

calorimeter and adsorbent. Variations in the heat of adsorption of oxygen on a tungsten surface partially covered with hydrogen were also determined.

In determinations where the heat of adsorption is small, for instance inert gases on solids, it becomes necessary to find some means, other than the calorimetric one, for measuring the heat produced. Such methods are usually termed indirect, as the heat of adsorption is calculated from the pressure and amount adsorbed using the well known Clausius Clapeyron equation. This equation is applicable to systems in equilibrium; in this case it gives a relation between the equilibrium pressure, temperature and heat of adsorption for a definite surface covered or constant amount adsorbed.

At equilibrium

$$\left[\log_{10} \frac{P_1}{P_2} \right]_{\theta} = - \frac{2.303 \Delta H}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Where P_1 and P_2 are the pressures of the adsorbing gas at temperatures T_1 and T_2 respectively, which produce a definite fraction of surface covered θ . ΔH is the heat of adsorption per gram molecule of gas adsorbed and R the gas constant.

Orr (10) used this method to determine heats of adsorption of inert gases on salt crystals. Even at the low temperatures at which he worked, the adsorption as well as the

heat of adsorption is small. Isotherms are determined at several different temperatures and the heat of adsorption is calculated from these, using the Clausius Clapeyron equation.

In the present investigation the heat of adsorption of the upper layer of oxygen on tungsten is determined by means of the latter method. Isotherms are determined at two different temperatures, approximately 25°C and 100°C .

The 25°C isotherm has already been determined in connection with Morrison and Roberts (9) work on the general features of the oxygen film on tungsten. In order to determine the isotherm at 100°C certain changes in the apparatus were necessary. These changes, along with the consideration that the tungsten filament has not necessarily the same surface area, make it desirable to redetermine at the same time the 25°C isotherm.

THE ACCOMMODATION COEFFICIENT METHOD OF MEASURING ADSORPTION.

THE ACCOMMODATION COEFFICIENT METHOD OF MEASURING ADSORPTION.

The determination of any well defined isotherm required that the pressure of the gas, the temperature, the area of the solid surface and the amount of surface covered by the adsorbed gas be known. The first three factors are relatively easily determined but the extent of surface covered is often quite obscure.

In this work, the accomodation coefficient technique originally developed by Roberts (12) is used. The accommodation coefficient is a measure of the efficiency of interchange of heat between a metal surface and an impinging gas molecule. Knudsen (3) defines it in the following manner.

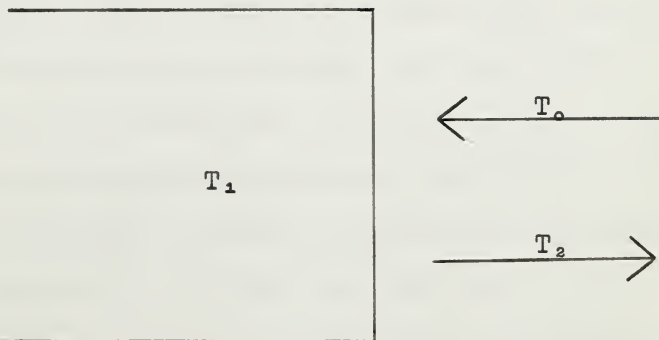


figure 1.

Consider a metal surface at a temperature T_1 and a gas molecule at a temperature T_0 (Fig. I). This molecule strikes the surface and rebounds at a temperature T_2 . Then the accommodation coefficient 'a' is equal to $\frac{T_2 - T_0}{T_1 - T_0}$ the ratio between the two temperature differences. If the temperature T_2 of the rebounding molecule is equal to T_1 , the temperature of the solid surface, the accommodation coefficient is equal to 1. As T_2 approaches T_0 , the temperature of the impinging molecule, the accommodation coefficient approaches zero.

Roberts (12) found the accommodation coefficient of an inert gas on a freshly cleaned tungsten surface to be considerably lower than previously had been indicated. In addition he found that it decreased with decreasing temperature, approaching zero at 0°K (13). At a constant temperature the value also was noticed to increase with time, but after heating to a high temperature, always returned to the same value. This suggested that the accommodation coefficient was very sensitive to the presence of an adsorbed film. The gases, neon and helium, used in his determinations are chemically inert and they do not adsorb on tungsten at ordinary temperatures. The increase in the accommodation coefficient with time must therefore be due to the presence of other adsorbed gases on the tungsten surface.

Roberts (14) used this fact to study the adsorption of known gases on tungsten filaments, the basic assumption being that the change in accommodation coefficient is proportional to the amount of gas adsorbed.

The accommodation coefficient is measured by using tungsten in the form of a fine wire, which is set up in an evacuated glass system and is made one arm of a wheatstone bridge arrangement. The wire is heated to a temperature T_1 by means of a small current, the gas being at a temperature T_0 .

The energy from this small current is dissipated in three ways. It raises the temperature of the wire above that of surroundings. At this temperature some of the energy is lost by radiation, some through the leads, and the remainder is lost to the gas by conduction.

Knudsen (3) relates the heat loss q_g to the gas, with the accommodation coefficient in the following manner.

$$q_g = \frac{1.74 \times 10^{-4} P}{\sqrt{MT}} a$$

Where M is the molecular weight of the monatomic gas, neon in this case, P is the pressure of the neon in dyne cm^{-2} and T is the absolute temperature of the gas.

The radiation and end loss is constant for any one temperature and temperature excess of the wire, so can be determined by an experiment in vacuo. The sum of the radiat-

ion and end losses and the heat loss to the gas gives the total heat loss of the wire. This total heat loss is related to the temperature excess of the wire as previously mentioned, so that if one is known the other may be determined.

The relation between $\bar{t}$, the temperature excess of the wire and χ , the temperature coefficient of resistance is

$$T_1 - T_0 = \bar{t} = \frac{r_1 - r_0}{\chi r_0}$$

where r_1 is the resistance of the wire at the temperature excess $\bar{t}$ and r_0 is the resistance of the wire at the temperature of the gas.

For each resistance r_1 , a value of the accommodation coefficient can be deduced. In an experiment, the change in resistance, and thus, the change in the accommodation coefficient with time is measured.

Figure 5 shows the initial drift of the accommodation coefficient with time for a clean wire at both 25°C and 100°C. The accommodation coefficient is always found to increase slowly with time, due to the presence of adsorbable gases in the system. The initial value at 100°C is found to be somewhat higher than that at 25°C, which is in agreement with results of previous investigations (13). The arrow indicates the time at which the gas to be adsorbed on the tungsten filament is admitted to the system.

In the present investigation, oxygen is admitted to a clean tungsten wire. The pressures required are of the order of from 10^{-5} to 10^{-8} m.m. Hg. To obtain and measure these extremely small pressures a new method, devised by Morrison and Roberts (9), is employed. By means of this method a supply of oxygen, at practically constant pressure, is available to the wire for periods of at least two hours.

CONTROL OF THE OXYGEN PRESSURE.

CONTROL OF THE OXYGEN PRESSURE.

It is essential that the pressure at the wire remain constant throughout a determination. As the adsorption of gas by the wire causes a decrease in pressure, a method employing a constant flow of gas past the wire forms the most satisfactory means of obtaining constant pressure.

The oxygen system (Fig. 2) consists of a large reservoir B connected to the main part of the apparatus by a capillary tube K. C, C' are charcoal traps which can be immersed in liquid air. W is the tungsten wire on which the adsorption takes place.

The pressure of oxygen at the surface of charcoal at liquid air temperatures is very nearly zero (Page 6, (9)). Oxygen diffuses from the reservoir B through the capillary tube to D, where it divides into two streams a and b flowing towards each of the charcoal traps where the oxygen is removed. The wire W is placed in the path of one of these streams of oxygen.

The design of the apparatus is such that the resistance to the flow of gas through the capillary tube is due mainly to collisions with the walls of the tube, collisions with neon molecules being only a correcting term. Conversely, the resistance to the flow of gas from D to the charcoal surface through

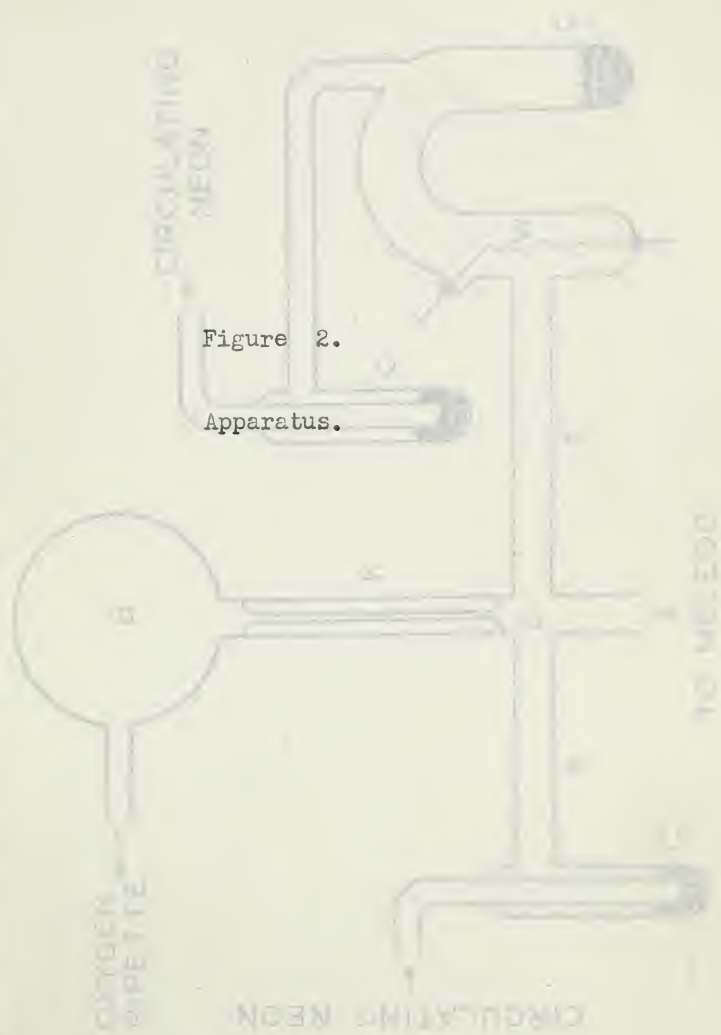
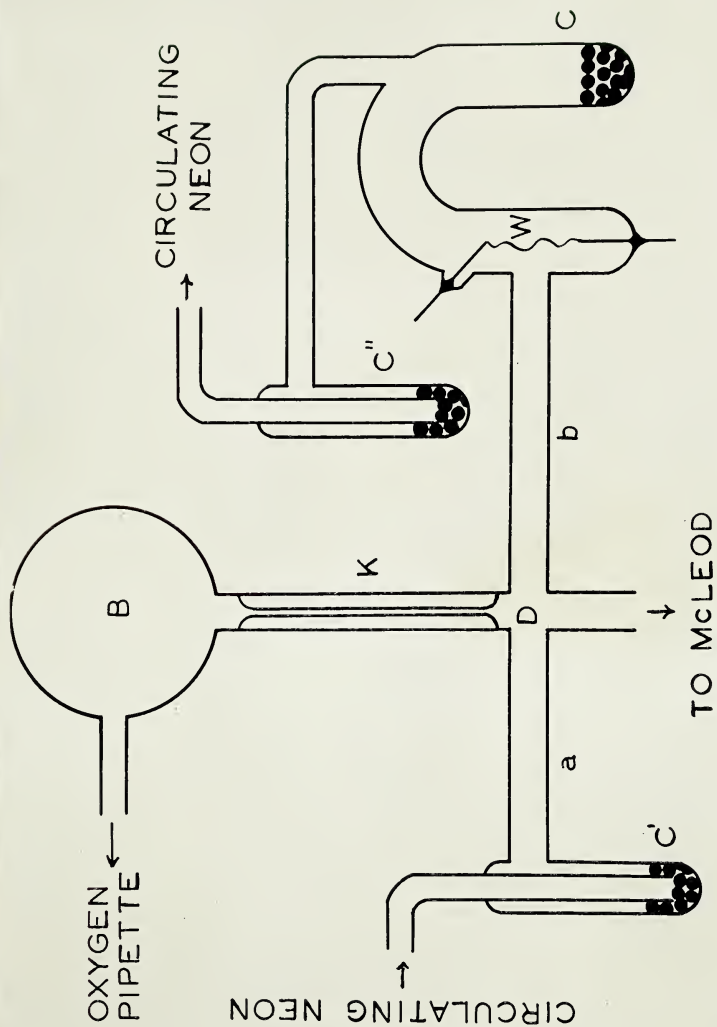


Figure 2.

Apparatus.

1790

1791



a and b is primarily due to collisions with neon molecules, a correction being applied for wall collisions.

It is known that the flow of gas through a tube is proportional to $\Delta P/R$ where ΔP is the total pressure drop and R is the sum of the resistances to that flow. At equilibrium the flow through the capillary tube equals the flow through from D to the charcoal traps. Then

$$\frac{\Delta P_t}{R_c} = \frac{\Delta P_d}{R_a} + \frac{\Delta P_d}{R_b}$$

where ΔP_t is the difference between the partial pressures at the two ends of the capillary. ΔP_d is the total pressure drop from D to the charcoal surfaces. ΔR_c is the sum of the resistances to flow through the capillary and R_a , R_b the sums of the resistances to flow in the respective tubes a and b.

Since all the molecules which strike the charcoal surface are not immediately adsorbed, the pressure at the charcoal surface is somewhat greater than zero. This effect can be represented as an additional resistance to the flow of oxygen, and appears as a correcting term in the denominator.

Corrections are also made for parts of the traps being at the temperature of liquid air, altering the effective length of the tubes.

For a definite pressure of neon, the ratio $\Delta P_d/\Delta P_t$

Figure 3.

Relation between P , the oxygen pressure at the wire and P_t that in the bulb B as a function of the neon pressure at both 25°C and 100°C .

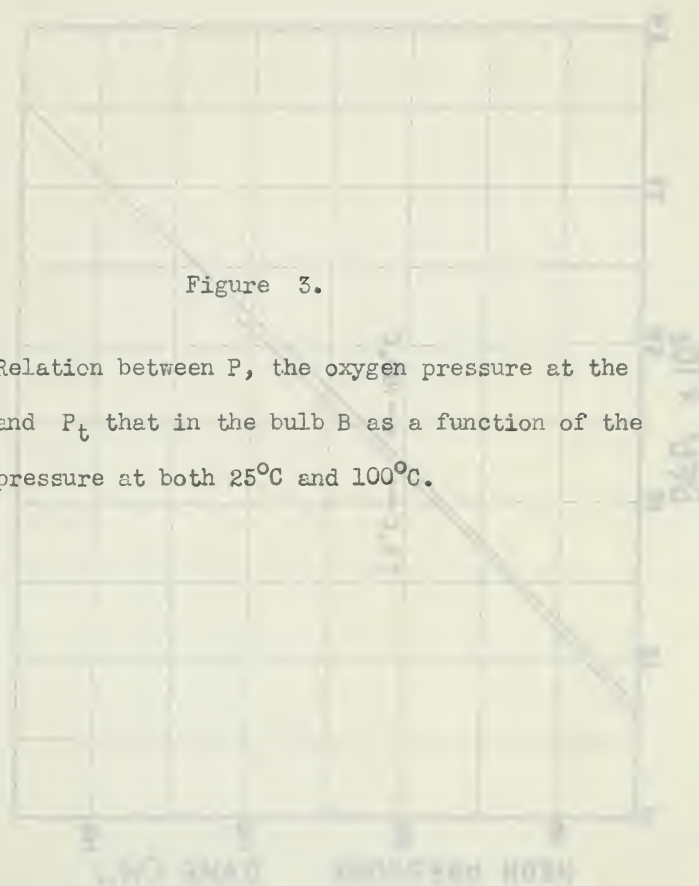
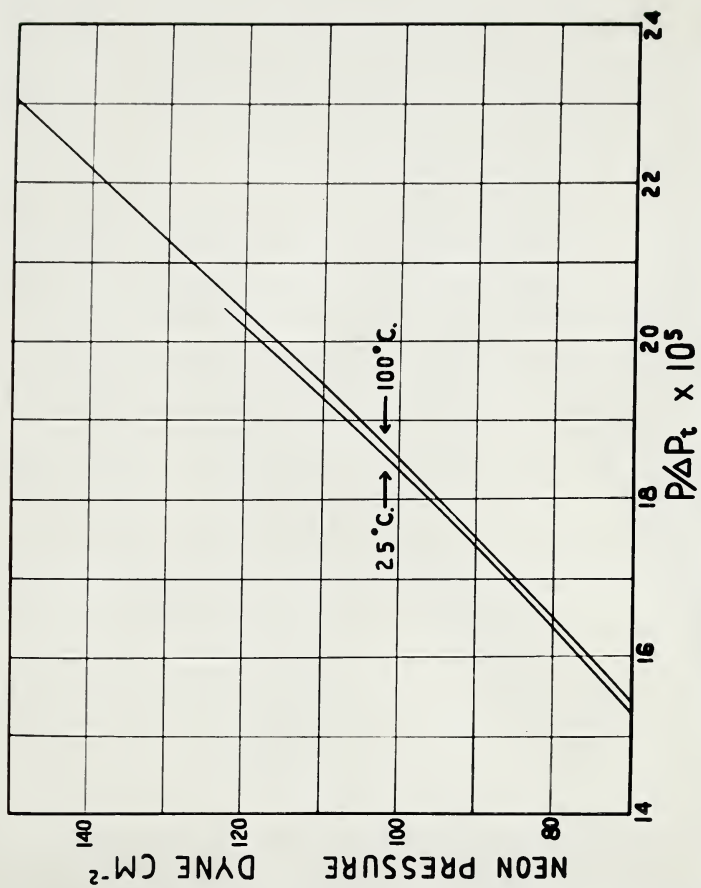


Figure 3.

Relation between τ , the oxygen pressure at 500
atm and P_2 atm in the case of a transition to low
mean pressure at both 500 and 1000.



can be calculated, knowing the dimensions of the tubes. Since in the pressure range used Δ^P_d is only 1/1000 the magnitude of Δ^P_t , it can be neglected in comparison. Δ^P_t is then the pressure in the calibrated reservoir B.

In terms of Δ^P_d , the pressure P at the wire is

$$\Delta^P_d \cdot \frac{R_{wc}}{R_{Dc}}$$

where R_{Dc} is the resistance to the flow of gas on the side b, from D to the charcoal surface where the pressure is zero. R_{wc} is the resistance to the flow of gas from the wire to the charcoal surface where the pressure is zero.

The ratio P/Δ^P_t is calculated for several definite neon pressures over the range used. This relation is represented in figure 3, and is specific for each apparatus used. From this, and knowing the oxygen pressure in the bulb B, the oxygen pressure at the wire is obtained for any known neon pressure.

APPARATUS AND EXPERIMENTAL PROCEDURE.

APPARATUS AND EXPERIMENTAL PROCEDURE.

The apparatus and method is essentially the same as that employed by Morrison and Roberts (9). Some alterations in dimensions were necessary in order to do experiments at 100°C. The length of wire used is 15.72 cm. as compared with 3.67 cm. and radius 3.19×10^{-3} cm. as compared with 5.55×10^{-4} cm. This altered wire cell is shown in figure 4.

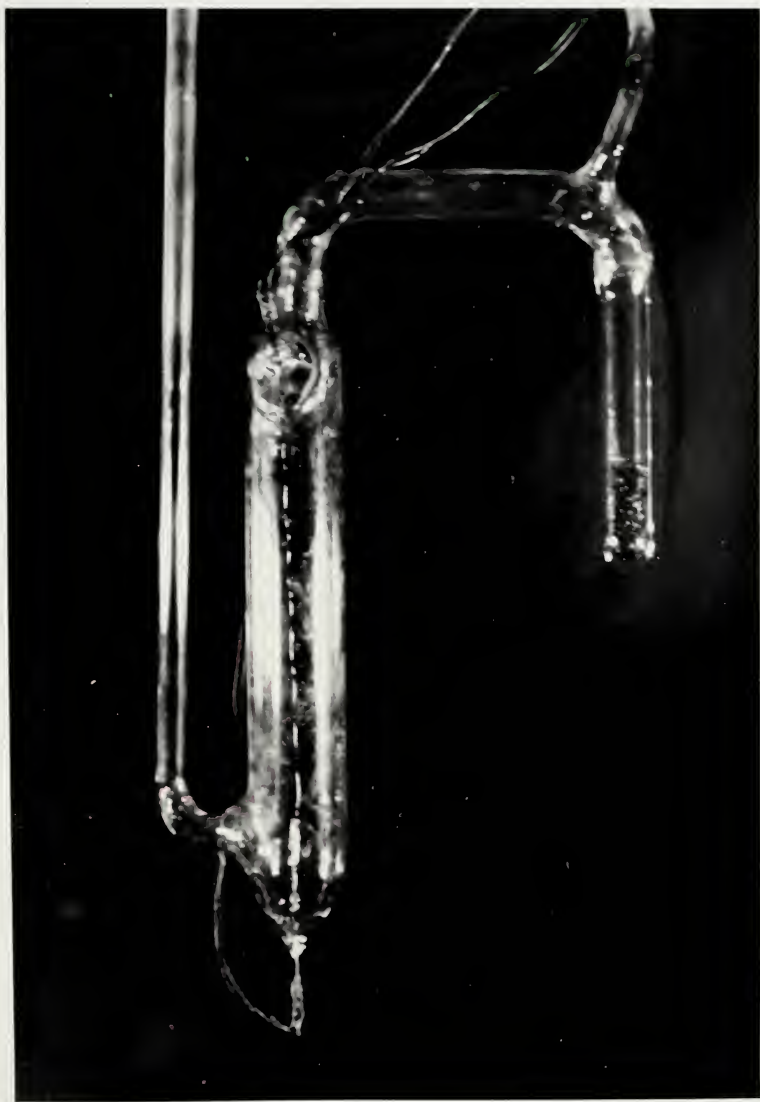
Before each experiment the charcoal and glass surfaces are thoroughly degassed by heating to approximately 300°C. The essential parts of the apparatus (Fig. 2) are then protected from mercury vapor and tap grease by liquid air traps beyond C' and C'', between K and B, as well as between D and the McLeod gauge. As soon as the best possible vacuum has been attained, the apparatus is shut off from the mercury diffusion and Hyvac pumps by means of mercury cut-offs. The charcoal traps C, C' and C'' are then immersed in liquid air, removing practically all the remaining gas by adsorption.

A measured sample of neon is purified by allowing it to remain in contact with charcoal at the temperature of liquid air. This is then admitted to the main system where it is continuously circulated through the charcoal traps C' and C'' for half an hour. This removes traces of adsorbable impurities

Figure 4.

The wire cell.







which might still be present on the glass surfaces. During this process of circulation a tube of larger dimensions is used to by-pass the capillary tube in order to hasten attainment of equilibrium throughout the system. Upon completion of the circulation, the by-pass is cut-off, leaving the capillary tube as the only connection between B and the wire cell.

The wire cell is completely immersed in a thermostated oil bath. In this bath, a special oil is used which has high insulating properties. The temperature of the bath is determined by means of a standardized thermometer, determinations being made at 24.8°C and 100.5°C .

The wire W forms one arm of a Wheatstone bridge which is arranged so that the other three arms may be shorted with suitable switches. By means of such an arrangement, a current sufficient to heat the filament to 2200°C can be passed through.

The filament is flashed at this temperature for two one minute periods. Between these flashings, the wire is allowed to cool for one minute. This gives sufficient time to enable the circulating neon to clean up impurities released from the wire by the flashing process.

In determinations at 100°C the neon is not kept circulating during the course of an experiment. Instead, the wire is flashed after the neon has circulated 20 minutes. The neon

is circulated for a further 10 minutes, allowing sufficient time for the adsorbable gas to be removed before it is stopped circulating. When the neon has come completely to rest, the wire is again raised to 2200°C for one minute. Then a small current (25 milliamperes), sufficient to raise its temperature 20° in excess of the oil bath, is passed through the wire.

As the neon is left circulating during each experiment at 24.8°C , the wire is flashed for two one minute periods after the neon has circulated for half an hour. The current is then reduced to the small value and the wire connected to the bridge. The change in resistance of the wire with time can be followed on the galvanometer scale.

The deflection of the galvanometer with time is recorded every 15 seconds, the value of the heating current being kept steady. If there is only a slight amount of adsorbable gas present, the initial drift of the galvanometer is very small. This drift is followed for a few minutes, sufficient readings being taken to insure an accurate extrapolation to zero time (Fig. 5).

At a definite time the oxygen, obtained by heating KMnO_4 , is released from a gas pipette into the two and one half litre reservoir B. Galvanometer readings are continued every fifteen seconds. As the adsorption approaches the equilibrium

state readings are taken less frequently, the final value being recorded 120 minutes after admission of the oxygen.

Neon pressures are measured with the McLeod gauge immediately before admission of oxygen as well as at the end of an experiment.

Galvanometer sensitivity and zero resistance r_0 is determined for each experiment. The latter is accomplished by measuring the resistance at 5 milliamperes and 25 milliamperes then extrapolating to zero current.

The temperature coefficient of resistance of the wire is determined for both of the bath temperatures used. This is accomplished by determining the zero resistance above and below each of the bath temperatures normally used. From these values the change of zero resistance with temperature can be plotted and χ , the temperature coefficient calculated from the slope.

Similarly radiation and end losses of the wire are determined for each bath temperature. To do this, the heat losses are measured with no gas present. This is done at three different temperature excesses so that the radiation and end loss for any temperature excess of the wire may be calculated.

EXPERIMENTAL RESULTS.

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The average values of the accommodation coefficient for the clean tungsten wire at the beginning of an experiment are 0.043 at 24.8°C and 0.048 at 100°C. A sharp rise in the value occurs upon admission of oxygen to the system, the rate of increase varying in the same direction as the oxygen pressure. The initial parts of two experiments are shown in figure 5, oxygen pressures being 2.83×10^{-5} dyne cm.⁻² for the 100°C experiment and 3.17×10^{-5} dynes for the 25°C experiment.

In each determination the accommodation coefficient reaches a fairly steady value about 120 minutes after admission of oxygen. Typical examples of this are shown in figure 6. Curve II is the accommodation coefficient-time relationship at 25°C, for an oxygen pressure of 3.17×10^{-5} dyne cm.⁻². Curves I and III show final values at 100°C for which the oxygen pressures are 5.88×10^{-5} and 1.3×10^{-5} dyne cm.⁻² respectively.

The obvious dip in curve I is a phenomenon common to all 100°C experiments at lower oxygen pressures. The value of the accommodation coefficient at the minimum, if it occurs, is consistently 0.183 irrespective of the pressure. The length of time that the accommodation coefficient remains at this minimum value, before starting to rise again, varies inversely with the

oxygen pressure. Also, the time taken to reach the minimum increases with decreasing pressure. The height to which the curve rises before dropping back to the value of 0.183 is dependent on the oxygen pressure, maximum effect being obtained at approximately 1×10^{-4} dyne cm.⁻² oxygen. At higher pressures the effect is reduced to a sharp levelling off, with a definite change in slope as the value rises again. At still higher pressures the effect is masked by rapid adsorption of oxygen by the wire and a resulting rapid rise in the value of the accommodation coefficient. At lower pressures than 1×10^{-4} dynes the effect is minimized by a slow change in the value of the accommodation coefficient with time. This is represented in curve III which has an oxygen pressure of 1.3×10^{-6} dynes. At this low pressure a value of 0.183 is only reached 120 minutes after admission of oxygen. Indications are that it would take several hours for an equilibrium value to be reached.

A suggestion of a similar phenomenon at 25°C is shown over a restricted pressure range. This takes the form of a quick change of slope in the accommodation coefficient-time curve, as shown in curve II figure 6.

In a normal experiment the value of the accommodation coefficient does not change greatly beyond 120 minutes after

the wire has been cleaned. Final values a_f , at 120 minutes, are determined for several oxygen pressures both at 24.8°C and 100.5°C. These are given in Tables I and II.

The flow of gas through the capillary cannot be accurately calculated when the mean free path of the gas becomes less than the diameter of the capillary tube. This is true for pressures above 1.5×10^{-2} dyne cm.⁻²; so that the last two results shown in Tables I and II give only an approximate measure of the pressures. The method of dosing oxygen, however, insures that these are about 5 times and 10 times the pressure of the last accurate result (Page 9(9)).

Some of the values are plotted against the oxygen pressure in dyne cm.⁻². The pressure spread as seen in Table I, makes it impossible to plot all the values of a_f 's in one diagram. For comparison the isotherm determined by Morrison and Roberts (9) at 25°C is included as curve III in figure 7.

The best extrapolations for the 24.8°C isotherm are $a_f = 0.1845$ at zero pressure and $a_f = 0.330$ at maximum pressure. Corresponding values for the 100.5°C isotherm are $a_f = 0.2008$ and $a_f = 0.360$.

Letting θ be the fraction of available sites covered and assuming that θ changes linearly with change in the accommodation coefficient, these values then correspond to $\theta = 0$, no upper film, and $\theta = 1$, the complete upper film respectively.

Table I - 24.8°C.

Date of Experiment	Pressure at Wire : Dyne cm. ²	Log Pressure	a _f	θ	t
March 19	1.235 x 10 ⁻⁵	5.092	0.1906	0.0419	15.0
" 14	3.167 x 10 ⁻⁵	5.501	0.1988	0.0983	15.9
" 15	7.623 x 10 ⁻⁵	5.882	0.2120	0.1890	15.5
" 26	7.718 x 10 ⁻⁵	5.887	0.2102	0.1766	15.3
" 27	1.578 x 10 ⁻⁴	4.198	0.2210	0.2508	15.2
" 28	2.514 x 10 ⁻⁴	4.400	0.2272	0.2934	14.6
" 30	7.190 x 10 ⁻⁴	4.856	0.2420	0.3952	13.7
" 13	3.157 x 10 ⁻³	3.499	0.2640	0.5464	12.4
Feb. 6	3.996 x 10 ⁻³	3.602	0.2715	0.5980	11.9
March 16	9.486 x 10 ⁻³	3.977	0.2845	0.6872	
" 27	5.4 x 10 ⁻²	2.73	0.3049	0.8274	
" 28	9.4 x 10 ⁻²	2.97	0.3177	0.9154	

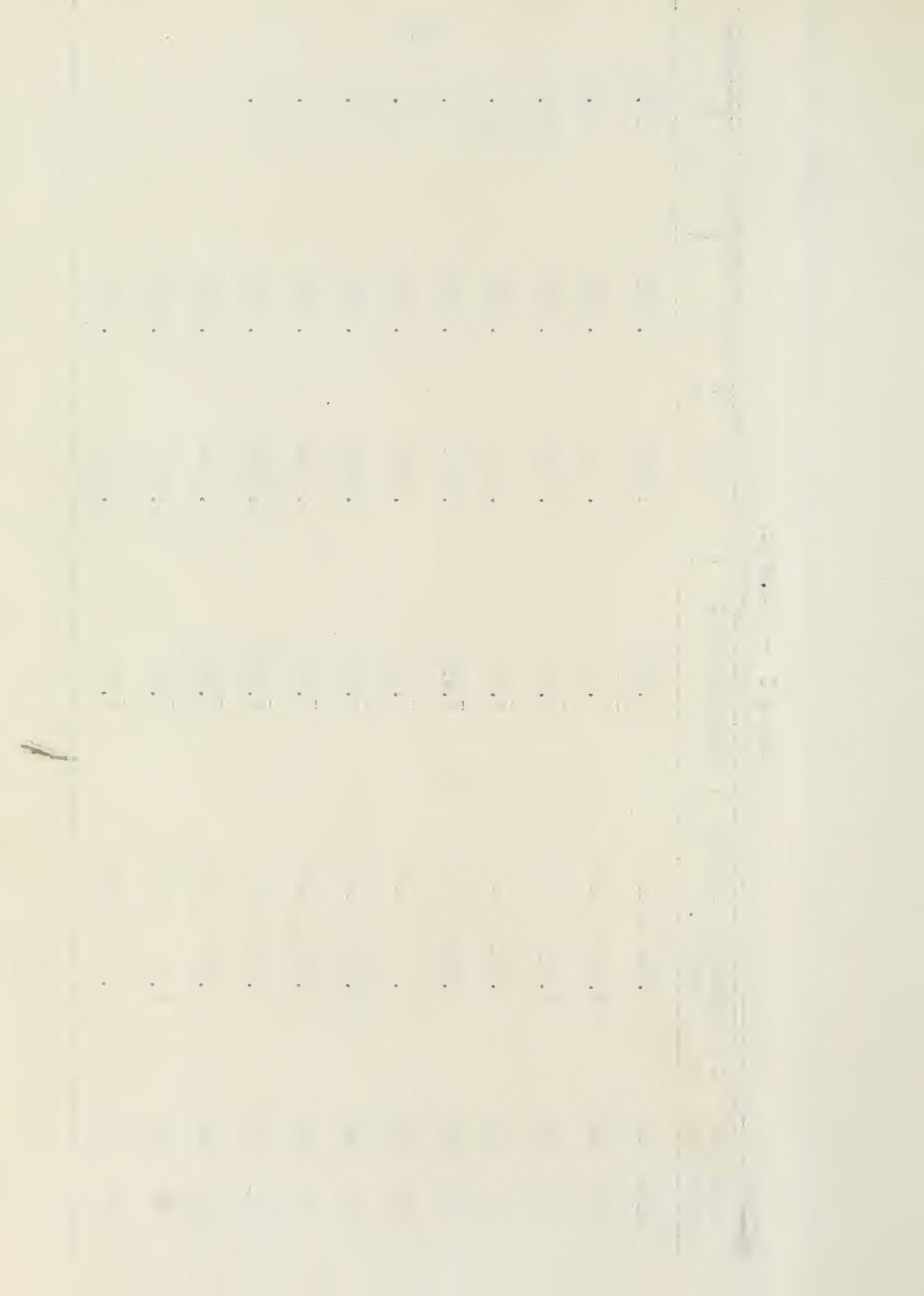


Table II - 100.5°C.

Date of Experiment	Pressure at Wire : Dyne cm. ²	Log Pressure	a _f	θ	t
Feb. 24	2.830 x 10 ⁻⁵	5.452	0.2085	0.0484	21.0
March 23	5.884 x 10 ⁻⁵	5.770	0.2152	0.0904	18.8
Feb. 11	7.549 x 10 ⁻⁵	5.878	0.2175	0.1050	18.6
March 24	1.155 x 10 ⁻⁴	4.063	0.2213	0.1288	18.6
April 2	4.228 x 10 ⁻⁴	4.626	0.2402	0.2476	16.4
" 3	1.081 x 10 ⁻³	3.034	0.2580	0.3594	17.0
" 5	3.486 x 10 ⁻³	3.542	0.2887	0.5522	15.7
March 25	7.735 x 10 ⁻³	3.888	0.3110	0.6922	15.0
Feb. 18	1.351 x 10 ⁻²	2.131	0.3200	0.7488	
April 2	8.0 x 10 ⁻²	2.90	0.3350	0.8430	
" 3	1.3 x 10 ⁻¹	1.12	0.3472	0.9196	



Thus for 24.8°C experiments:

$$\theta = \frac{a_f - 0.1845}{0.33 - 0.1845}$$

and for the 100.5°C experiments:

$$\theta = \frac{a_f - 0.2008}{0.36 - 0.2008}$$

Using these, values of θ for each a_f are calculated and shown in Tables I and II. Some of these are plotted in figure 8. As before, pressure spread prevents all of the values being plotted. At low values of θ the 100.5°C curve lies below the 24.8°C curve, the two approaching each other at a value of $\theta = 0.5$. In order to represent the complete isotherm in one diagram the pressure range was compressed on a logarithmic scale. In figure 9, θ is plotted against $\log P$ for both temperatures at which determinations were made. In addition the values of θ obtained by Morrison and Roberts (9) are plotted as points for comparison.

Dimensional considerations of the tungsten lattice and oxygen molecule area previously indicated that there is only sufficient space for half the available sites to be covered with oxygen molecules (fig. 10). Such a molecular layer would then be completed at $\theta = 0.5$ (page 10, fig. 4 (9)). To plot these values on the same chart one scale is superimposed on the

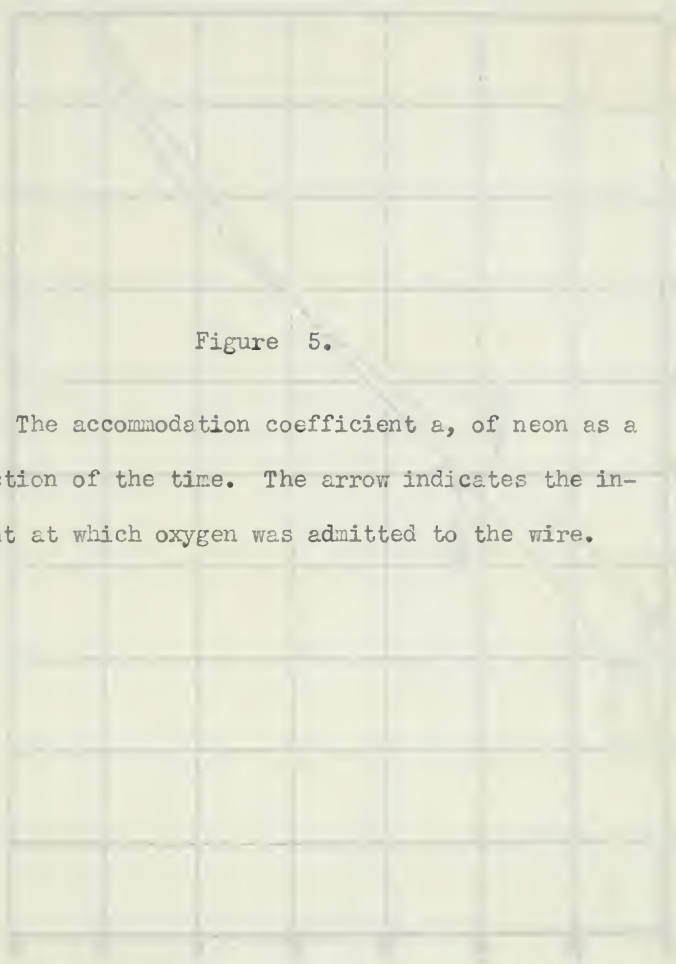


Figure 5.

The accommodation coefficient a , of neon as a function of the time. The arrow indicates the instant at which oxygen was admitted to the wire.

Figure 5.

The recommended coefficient α of neon as a
function of the time. The arrow indicates the in-
stant at which oxygen was admitted to the tube.

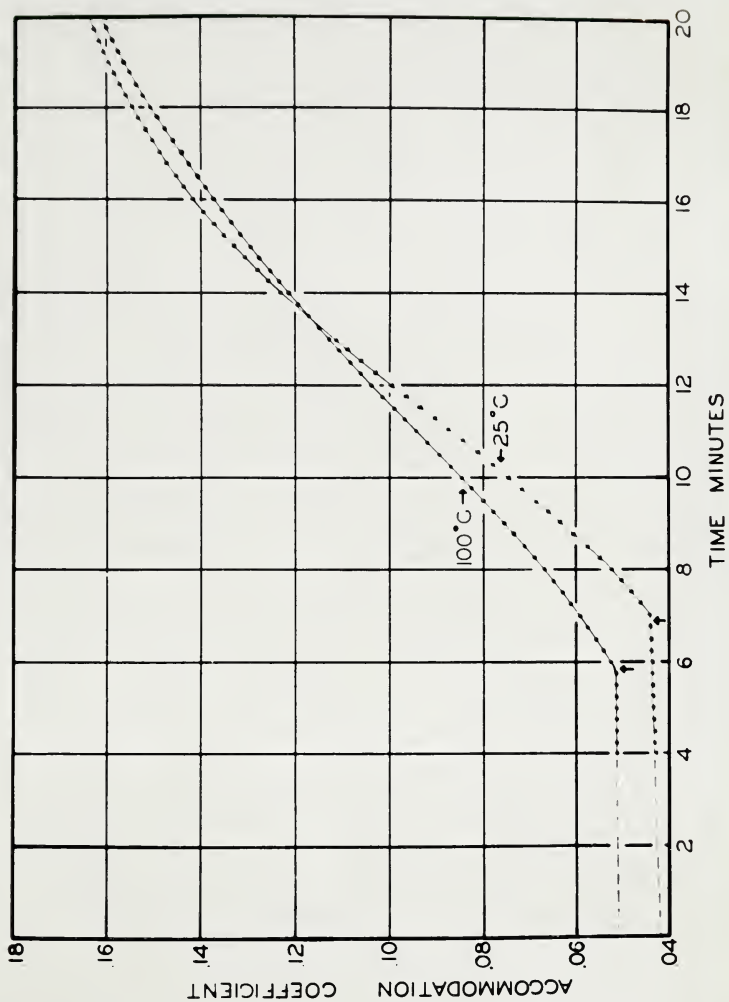


Figure 6.

The accommodation coefficient a , of neon as a function of the time.

Curve II - 24.8°C .

Curve I and III - 100.5°C .

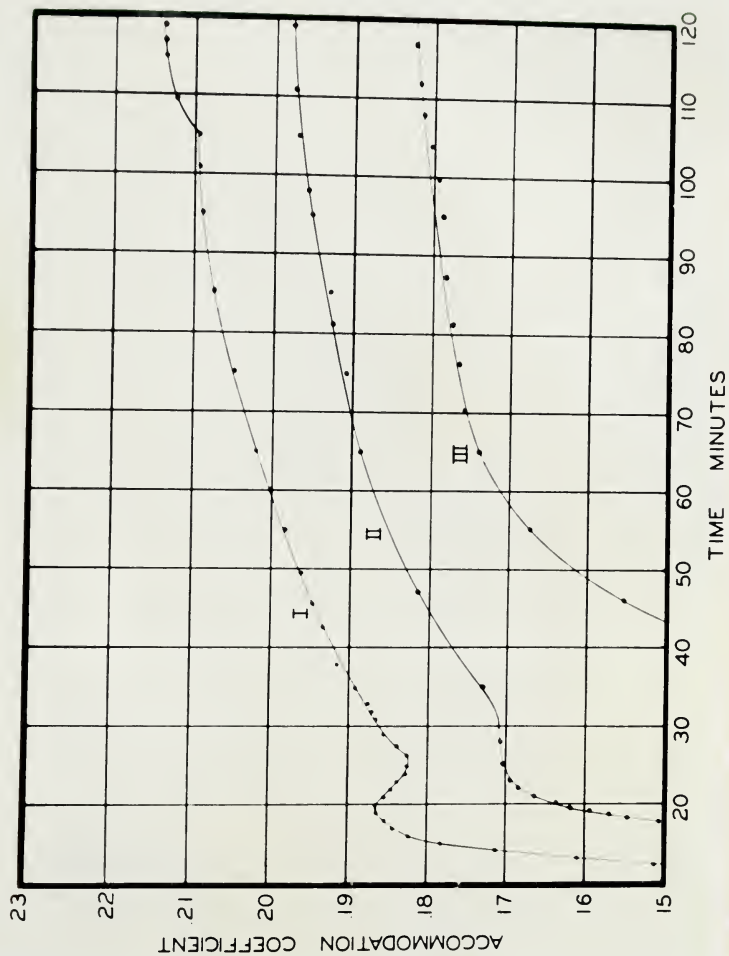
Figure 8.

The meteorological conditions at the time of the

eruption of the lake.

Curve II - 24.8°C.

Curve I and III - 20.0°C.



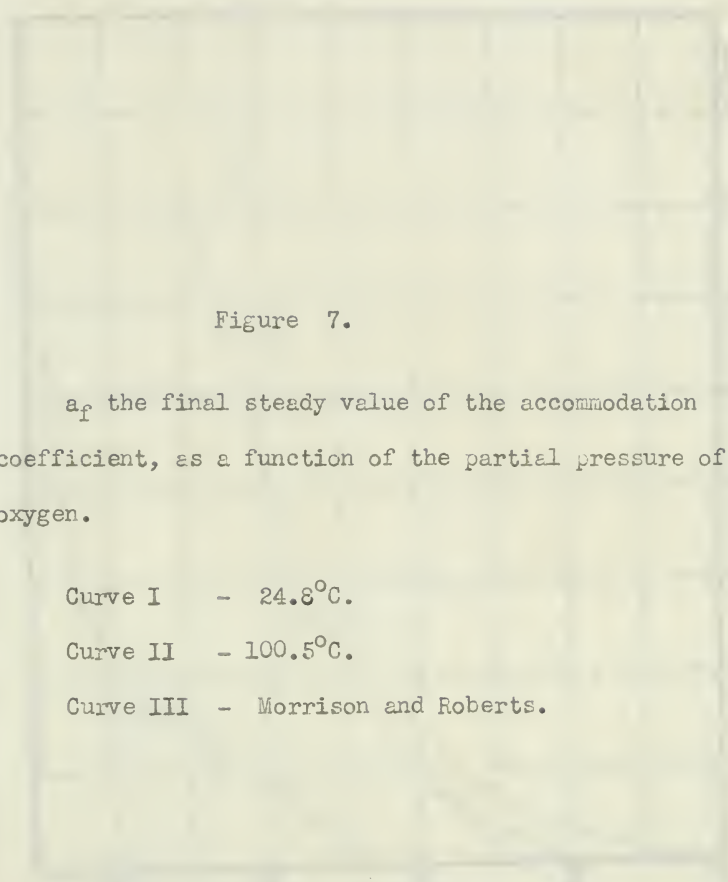


Figure 7.

a_f the final steady value of the accommodation coefficient, as a function of the partial pressure of oxygen.

Curve I - 24.8°C .

Curve II - 100.5°C .

Curve III - Morrison and Roberts.

Figure 2.

of the final steady value of the concentration
characterized as a function of the initial pressure of
oxygen.

Curve I - 25.5%
Curve II - 100.5%
Curve III - 200.5% and 400.5%.

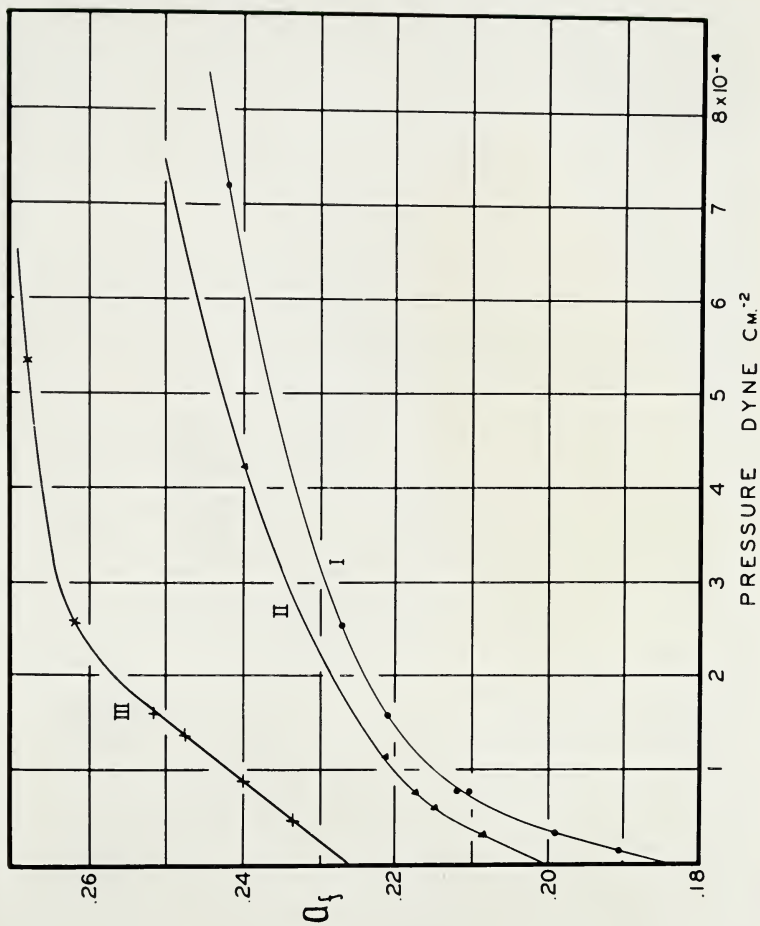


Figure 8.

θ , the fraction of sites occupied in the upper layer
as a function of the partial pressure of oxygen.

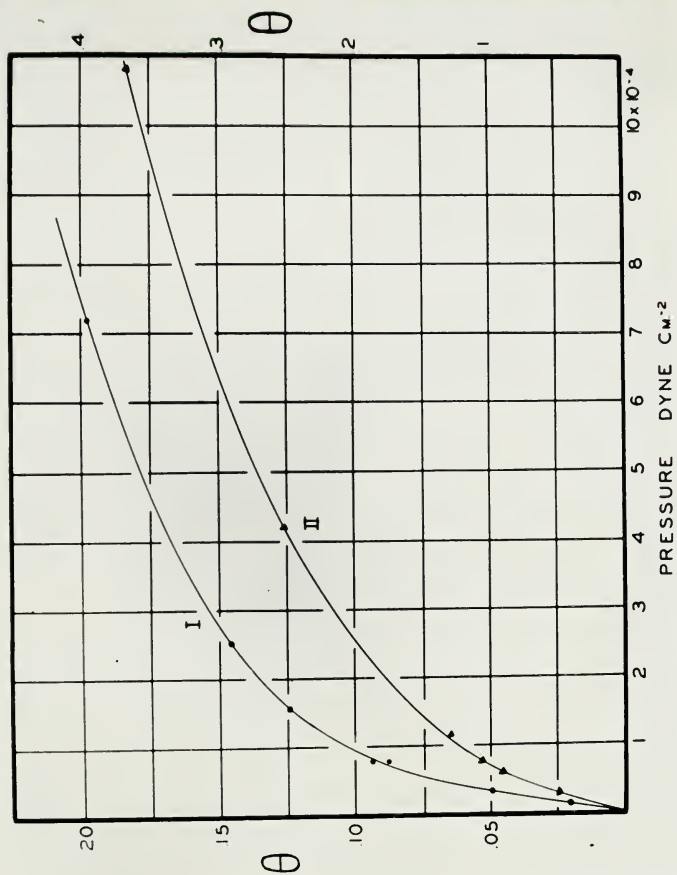
Curve I - 24.8°C.

Curve II - 100.5°C.

Figure 3.

8, the fraction of sites occupied in the upper layer
as a function of the partial pressure of oxygen.

Curve I - 24.8°C.
Curve II - 100.2°C.



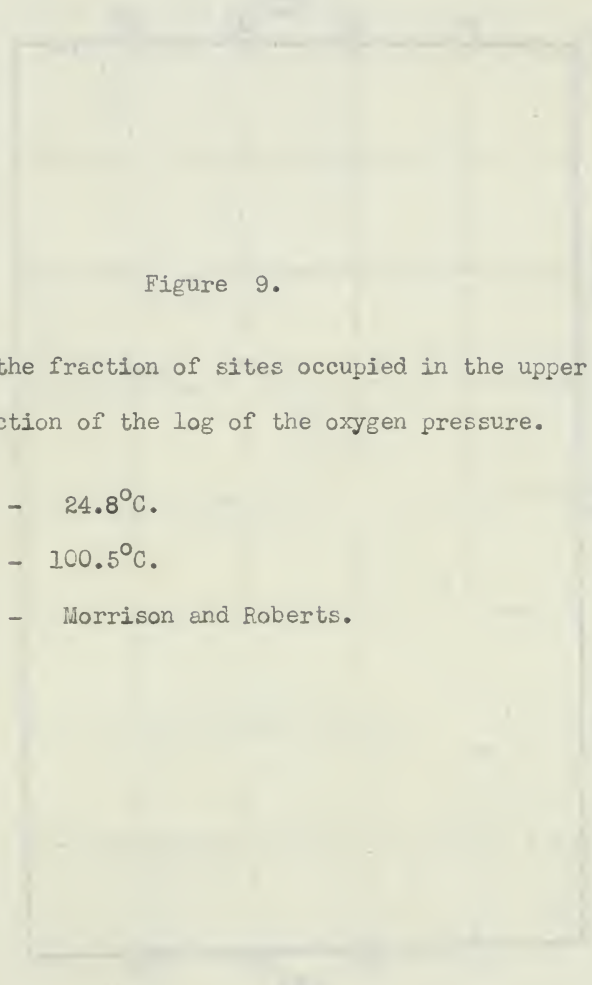


Figure 9.

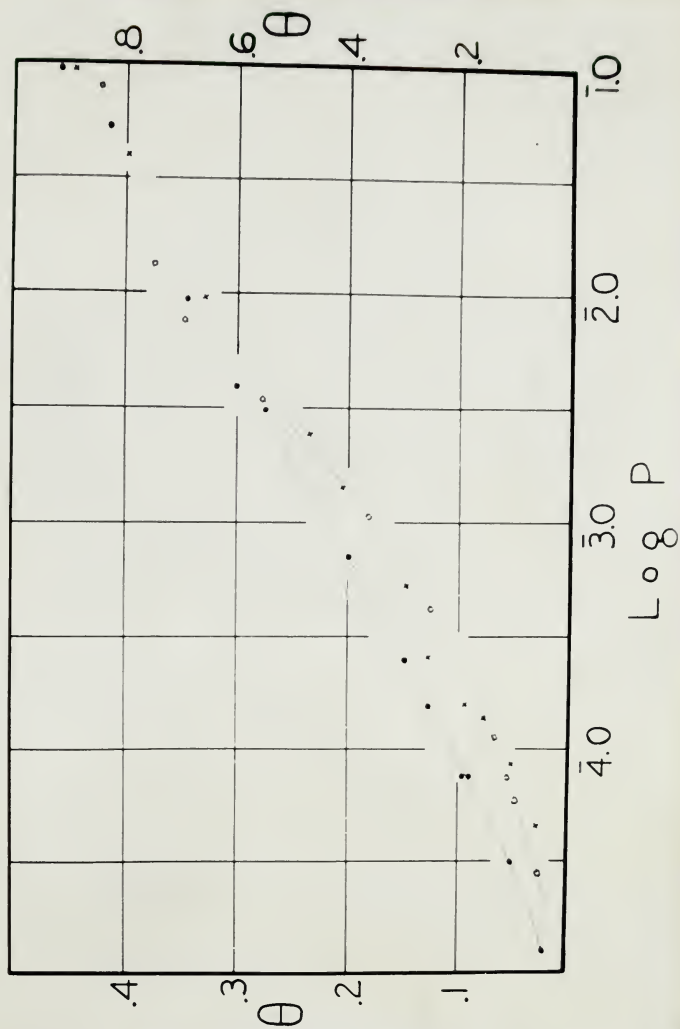
θ , the fraction of sites occupied in the upper layer
as a function of the log of the oxygen pressure.

- - 24.8°C.
- ◻ - 100.5°C.
- x - Morrison and Roberts.

Figure 2.

6. The fraction of sites occupied in the upper layer
is a function of the top of the oxygen pressure.

22.8°C.	-	.
100.0°C.	-	3
Marshall and Roberts.	-	x



other. Effectively this multiplies all the values obtained by Morrison and Roberts by 2.

Figures 8 and 9 are actually forms of adsorption isotherms. From these isotherms, corresponding pressures are taken for constant values of θ and substituted in the Clausius Clapeyron equation (page 7).

In the following calculation, the heat of adsorption is given at $\theta = 0.2$ the pressures are 9.3×10^{-6} and 2.48×10^{-4} dyne cm.⁻² for 24.8°C and 100.5°C respectively. As the temperature of the wire is above that of the bath, an average value for the temperature excess of the wire is added to the bath temperature of each isotherm.

Table III

θ	: ΔH cal./gm. mol.
0.1	416
0.15	532
0.2	566
0.25	535
0.30	516
0.35	465
0.40	382
0.50	232

$$\text{Thus } T_2 = (373.6 + 18.3) = 391.9^\circ \text{K.}$$

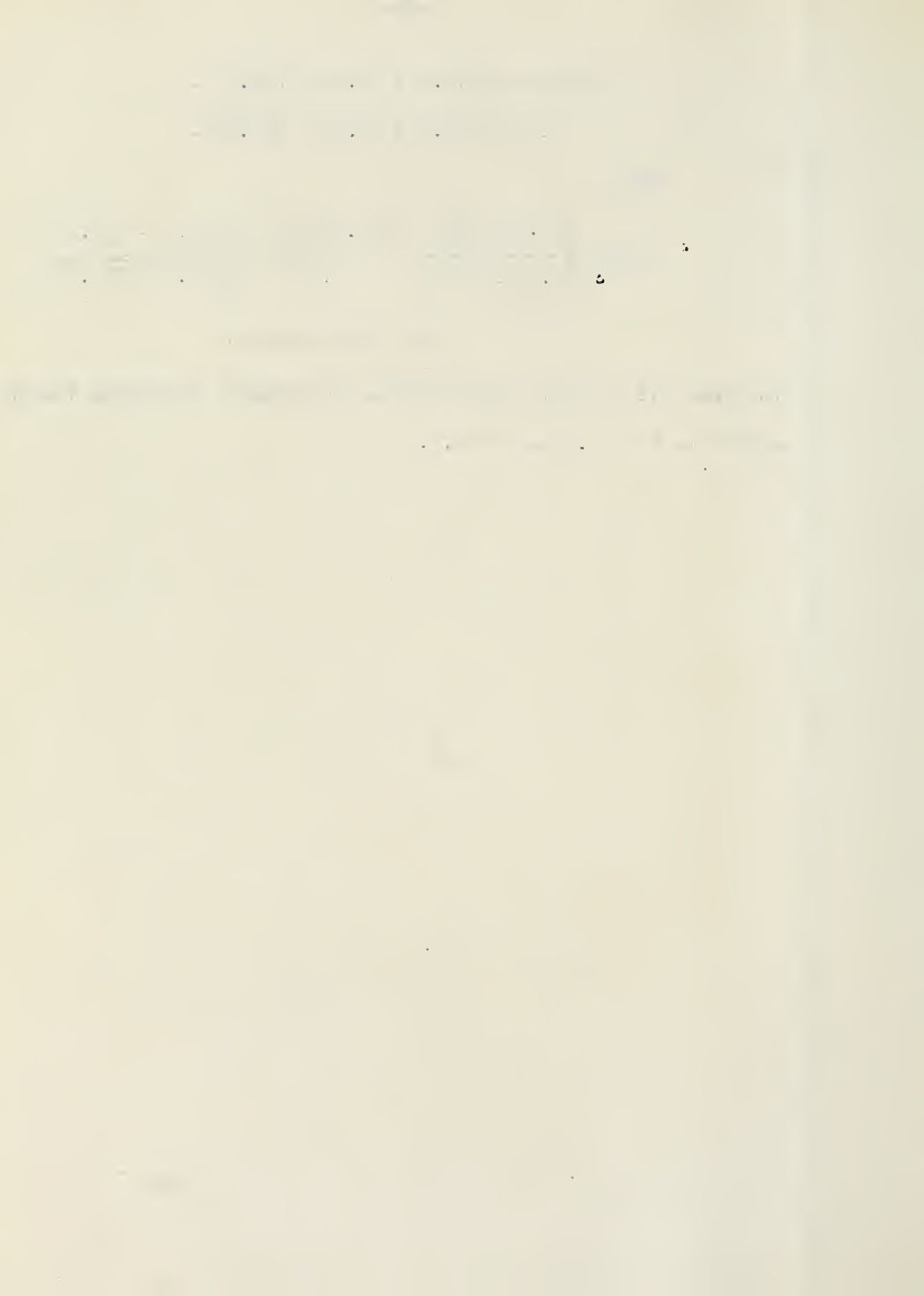
$$T_1 = (297.9 + 14.4) = 312.3^\circ \text{K.}$$

Then

$$\log_{10} \left[\frac{9.3 \times 10^{-5}}{2.48 \times 10^4} \right] = \frac{-2.303 \Delta H}{1.987} \left[\frac{391.9 - 312.3}{391.9 \times 312.3} \right]$$

$$\Delta H = 566 \text{ calories.}$$

In Table III are given the heats of adsorption at several values of θ from $\theta = 0.1$ to $\theta = 0.5$.



DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS.

The values of the accommodation coefficient for the clean wire are of the correct order of magnitude. The value $a = 0.043$ at 24.8°C compares with 0.057 for the wire used by Morrison and Roberts (9). A different roughness factor would account for the observed difference which is always found when different wires are used (14). The higher value $a = 0.048$ obtained at 100°C for the same wire confirms the observation of Roberts (13) and Van Cleave (16).

The final values reached by the accommodation coefficient in 120 minutes are given in Tables I and II and are plotted in figure 7. As has been shown in the work of Morrison and Roberts (9) the first film on tungsten is composite and probably is made up of oxygen atoms directly over tungsten sites, with a percentage of sites occupied by oxygen molecules. The irreversibility of the adsorption of this first and composite film is shown by its high heat of adsorption (14) and the fact that it forms at any pressure of oxygen. The amount of oxygen in the film above this composite, initial film depends on the pressure, and the value for the accommodation coefficient obtained by extrapolation to zero pressure will give a bare upper film (in other words a film with $\theta = 0$). This has been done at both

temperatures in figure 7. It will be seen that the 100°C extrapolation is farther than that at 25°C. This was necessitated by the fact that an experiment at 100°C and pressure of 1.3×10^{-5} dyne cm. $^{-2}$ (curve III fig. 6) did not go beyond $\alpha = 0.183$ in 120 minutes. This is quite consistent with other observations at 100°C, which will be discussed later, but nullifies this determination in so far as the final isotherm is concerned.

At the highest pressures α_f seems to be coming to a steady value, at which $\theta = 1$, the complete upper film. Following Morrison and Roberts (9), extrapolations are made to what appear to be the final values attainable. This requires carrying out determinations whose pressures are not known accurately, but are of the order of 5 and 10 times the highest pressure accurately measurable.

The relative positions of the α_f 's for the 25°C and 100°C indicate that at the highest pressures the film is approximately of the same population at 100°C as at 25°C. For instance, if the ratios of the accommodation coefficient at 25°C to those at 100°C for the clean wire, for the wire without upper oxygen film and for the complete upper film respectively, are compared, similar results are obtained.

$$0.043/0.048 = 0.900,$$

$$0.1845/0.2008 = 0.922,$$

$$0.330/0.360 = 0.917,$$

Thus the extrapolated values $a_f = 0.330, 0.360$ become equal to $\theta = 1$.

θ is calculated for each intermediate a_f , assuming a linear relation between θ and the change in a_f . The initial values of θ are not very sensitive to the final value of a_f chosen as the extrapolation, but are very sensitive to the initial extrapolation. The importance of this extrapolation is emphasized when θ is plotted against the log of the pressure as in figure 9. The crosses shown are the values obtained by Morrison and Roberts. If one examines the initial a_f 's obtained by Morrison and Roberts (curve III, fig. 7), it will be seen that they vary linearly with pressure. The present results do not confirm this, and as these give a self consistent log P - θ curve, as well as being carried out with lower oxygen pressures, it is considered that they are more reliable. Moreover, the Morrison and Roberts values give inconsistent variability in the log P - θ curve. A somewhat different initial a_f , for $\theta = 0$, would straighten out the initial part of their results.

Before discussing the shapes of the isotherms and the

values obtained for the heat of adsorption, it is convenient to introduce and discuss recent theoretical and experimental material concerning nature of forces between adsorbed particles and adsorbing surfaces.

Several theoretical papers have been published in recent years, which attempt to account for adsorption forces. Lennard-Jones (8) draws attention to the variation of adsorption with temperature. For instance in the case of hydrogen, with certain metals there is considerable adsorption at very low temperatures, diminishing to a minimum between -180°C and 0°C , and increasing again to a maximum, followed by another minimum, and at very high temperatures a third maximum. Here, there appears to be at least three different kinds of adsorption. The first type, at very low temperatures, is usually called van der Waals adsorption, being due to van der Waals forces; the second type is called "chemisorption" or "activated" adsorption, requiring a certain temperature to permit its occurrence.

Further, Lennard-Jones (7) shows that the cohesive forces between atoms and molecules also fall into definite categories. All rare gases are monatomic and difficult to liquefy. Hydrogen, oxygen and nitrogen are diatomic stable molecules at room temperatures; oxygen for instance requires 117,000 cal./gm. molecule to dissociate into atoms. The forces holding

together the atoms in these homopolar molecules are very large. Yet these molecules are like the monatomic inert gases in resisting liquefaction. However they do eventually cluster to form liquids, the heat of evaporation for oxygen being 1,630 cal./gm. molecule at its boiling point, and for argon 1500 calories. The attractive forces between argon atoms in liquid argon and oxygen molecules in liquid oxygen are similar in magnitude as both are electrically symmetrical particles.

The next step is the assumption that forces operating between like atoms are similar to those operating between different atoms. That is, there should be categories of adsorption heats paralleling cohesive energies between like atoms. This is born out by experience. Heats of adsorption of the order of 50,000 to 150,000 cal./gm. molecule are observed, and on the other hand heats as low as 500 to 3,000 cal./gm. molecule are observed. The latter occur in low temperature adsorption. Presumably the higher heats are associated with chemisorption and the lower ones with forces related to van der Waals attractions.

Lennard-Jones (1) has examined the second virial coefficient in the equations of state of various gases in order to determine the energy constants for these gases and from this the van der Waals energy. The van der Waals energy is of the form $-\frac{\mu}{r^6}$ (where r is the distance between the particles), and

arises from mutual induced polarization of the inert gas atoms or homopolar molecules. To complete the picture of the approach of two particles to each other, repulsive forces are considered, and are of the order of $\frac{1}{r^{12}}$. The net potential energy at a distance apart r becomes

$$\phi(r) = \frac{2}{r^{12}} - \frac{\mu}{r^6} \quad \text{and graphically}$$

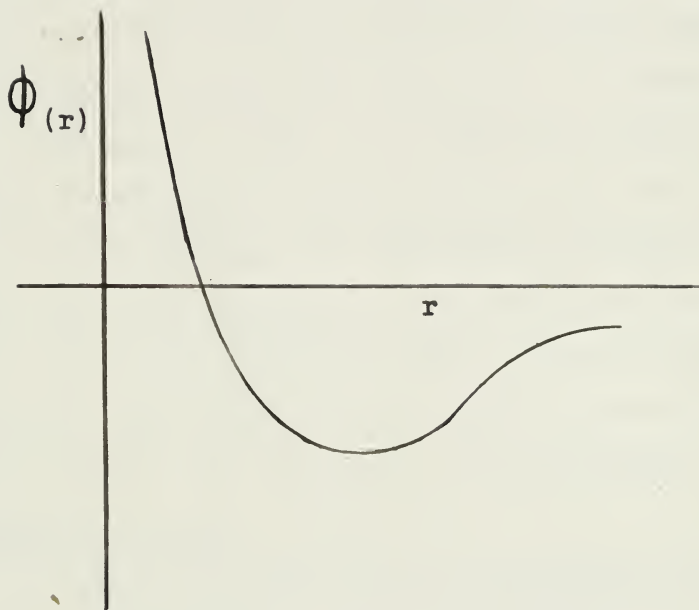


figure 10.

Such treatment gives good agreement with observed properties such as heats of sublimation and interatomic distances in the crystal. Moreover, the depth of the potential trough parallels the boiling points of the liquids, the more difficultly liquifiable having shallower troughs. In this way the nature of van der Waals forces has been quite clearly elucidated.

Applying the ideas of Lennard-Jones to low temperature adsorption Orr (11) calculated theoretically the adsorption behavior of argon on alkali halide crystals. This is an ideal system since there will be no tendency to chemical combination, and any cohesion between the inert gas and solid surface will be fairly simple in nature. He includes three terms in the energy of adsorption (1) the van der Waals potential (2) the electrostatic potential (3) the repulsive potential, in each case between the adsorbed atom and the crystal surface. A further consideration enters as the film is being built up to $\theta = 1$, namely the interaction between the induced dipoles (argon atoms held by van der Waals attraction) - which interaction may be positive or negative.

In a later paper (10) on the adsorption of non polar gases on alkali halide crystals, he determined the heats of adsorption from very low temperature isotherms. He found

complete confirmation for his theoretical treatment. In the case of the adsorption of oxygen on KCl, up to $\theta = 1$ the heat of adsorption was from 1,700 to 2,200 cal./gm. molecule, and it fell asymptotically above $\theta = 2$ (2 molecular layers of oxygen) towards the heat of vaporization of oxygen (1,750 cal./gm. molecule at the temperature of measurement). This means that the interactions between oxygen and the surface becomes negligible beyond 3 or more molecular diameters, and the adsorption becomes a form of liquefaction.

In the present work, the average magnitude of the heat of adsorption for oxygen on top of the first film is about 530 cal./gm. molecule. This clearly points to van der Waals adsorption. No comparison can be made to theoretical values because the force constants for oxygen are not worked out. However, some speculation is possible.

Resistance to adsorption can arise from lateral repulsions of the induced dipoles (6) and the temperature or kinetic energy of the gas molecule. Above 300° to 400°K the upper film begins to become unstable (14) and between that and 1100°K there is a temperature above which, no matter what the pressure of oxygen, the upper film cannot exist even in part. This may be called the critical temperature of the film, to compare it to the critical temperature of a liquid, above which the

thermal energy resists any cohesion irrespective of the magnitude of the pressure.

The critical temperature of oxygen is -118.2°C . Above this temperature the heat of vaporization is zero, and the kinetic energy is greater than the cohesive energy. Orr (10) carried out experiments at a much lower temperature than this so the thermal or kinetic energy is negligible in comparison to the cohesive. At this low temperature adsorption is favored rather than reduced by the temperature.

The present isotherms are for oxygen molecules on top of oxygen atoms which in turn are on top of tungsten. At the temperature at which the present experiments are carried out, the lateral interaction forces, if existent, would be positive. The thermal energy itself would oppose the van der Waals attraction to the underlying oxygen atoms and consequently only small heats of adsorption may be expected.

The variation in the heat of adsorption observed up to $\theta = 0.15$ is not significant because it depends too much on the extrapolation of the 100°C isotherm to zero pressure, which extrapolation is fairly large. Beyond $\theta = 0.15$ the heat of adsorption is about 530 calories, and it begins to decrease significantly beyond $\theta = 0.32$ until it is less than half at $\theta = 0.5$. Beyond

$\theta = 0.5$. it is not easily determined but is never greater than 200 cal./gm. molecule. Actually, if one examines the $\log P - \theta$ curve (fig. 9) which give the complete isotherm in one diagram, it is seen that the character of the isotherm changes at about $\theta = 0.5$. This is very interesting and has a possible explanation.

It is confirmed by the 25°C isotherm obtained by Morrison and Roberts (shown by crosses in figure 9). Orr (10) finds a similar change over in adsorption of non polar gases on alkali halides. A minimum occurs in the heat of adsorption at $\theta = 0.5$ and this is confirmed by theoretical considerations. From $\theta = 0$ to $\theta = 0.5$, the gas molecules adsorb in the centres of the lattice cells, but as θ tends to unity, the arrangement passes over to a close packed hexagonal pattern.

It is possible that in the present case, oxygen adsorbs superimposed on tungsten atoms or in the centre of a set of 4 tungsten atoms (the same coverage would result in either case, the case chosen being one of minimum potential energy). But obviously (fig. 11) this is not the closest packing possible, and so after such a film has built up with an ordered square arrangement (assuming the 100 tungsten plane underlying) it would gradually change over to some close packed arrangement. Such a phenomenon could change the character of the isotherm and also the heat of adsorption. It will be noted that this interpretation

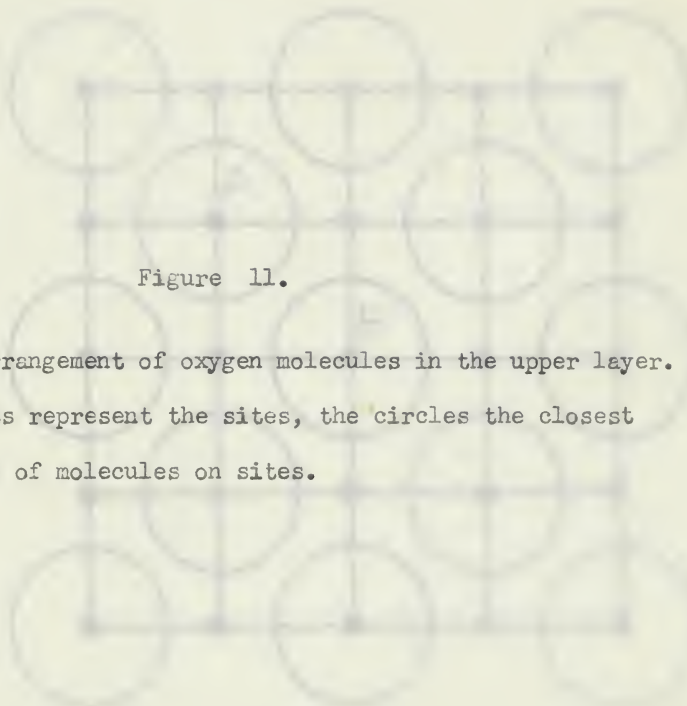
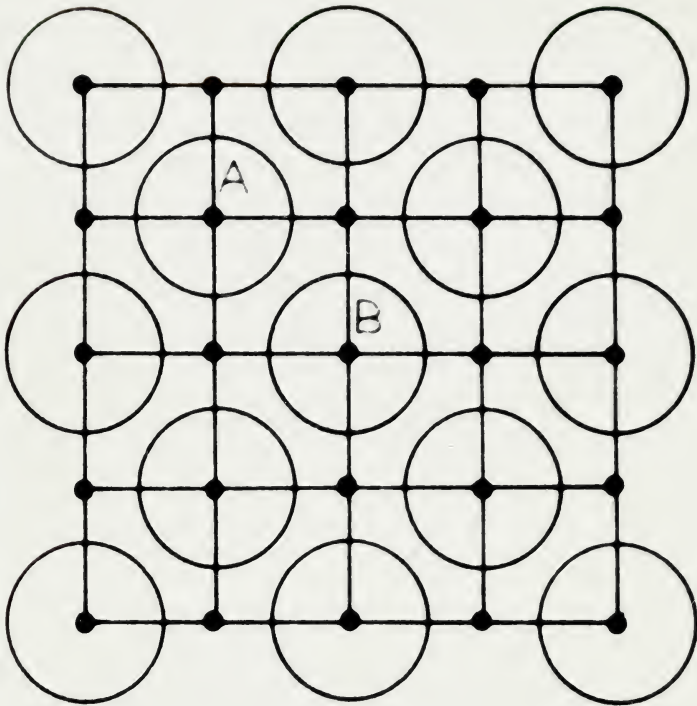


Figure 11.

Arrangement of oxygen molecules in the upper layer.
The dots represent the sites, the circles the closest
packing of molecules on sites.

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Arrangement of oxygen molecules in the upper layer.
The dots represent the sites, the circles the oxygen
packing of molecules on sites.



makes the complete film $\theta = 1$, not $\theta = 0.5$ as suggested by Morrison and Roberts (9).

Wang (17) calculated theoretical isotherms for the adsorption of molecules without dissociation on surfaces, with positive interactions (repulsion) between the adsorbed particles. That such repulsion can arise from the depolarizing effect of parallel dipoles on each other, is pointed out by Langmuir (6). Wang showed that such interaction affects the isotherm so that a relatively large increase in pressure is required to reach $\theta = 0.5$. In the present investigation it is found that a hundredfold increase in the pressure is required to change θ from 0.05 to 0.5, another hundredfold increase completing the film. With a negative or no interaction the isotherm would pass $\theta = 0.5$ with an increase of a few times the pressure which gives $\theta = 0.05$.

In summary, the heat of adsorption of oxygen in the upper oxygen film as measured from the isotherms determined at 25°C and 100°C indicate that molecular oxygen is adsorbed on top of the tightly held oxygen film on tungsten by means of van der Waals attractions together with lateral repulsions which become effective after the film is about one third complete.

SUMMARY.

SUMMARY.

Using the method of Morrison and Roberts, the change in the accommodation coefficient of neon on a tungsten surface, at both 24.8°C and 100.5°C , has been measured as affected by the adsorption of oxygen, over a pressure range of 1×10^{-6} to 10^{-1} dyne cm^{-2} .

From the final values obtained for every pressure determined, Pressure - a_f curves were plotted and extrapolated to zero and maximum pressure.

Using these extrapolations, θ the fraction of surface covered has been calculated for each pressure and plotted as isotherms.

The heat of adsorption has been calculated from the two isotherms at various values of θ using the Clausius Clapeyron equation.

The nature of the forces holding this second film to the atomic film as well as the variation in the heat of adsorption with θ , the fraction of surface covered, has been discussed and compared to the work of Orr (10) on alkali halide crystals.

APPENDIX.

APPENDIX.

Removal of the Second Film.

At 100.5°C , the extrapolation of the a_f 's to zero pressure gives a value of 0.2008 for the accommodation coefficient. The value of 0.183 at which the minimum occurs in the 100°C adsorption curves indicates a surface not completely covered by the first film. In order to fix the position of the minimum in the 100°C experiments, the accommodation coefficient is determined for a surface from which all molecular oxygen is removed.

To do this, the wire is heated to a temperature of approximately 1100°K for one minute in the presence of small oxygen pressure. The temperature of the wire is determined by measuring its resistance and calculating from the resistivity. The wire is allowed to cool and readings are taken for several minutes. Extrapolation to zero time (at which heating was stopped) gives the value of the accommodation coefficient at cessation of the heating. This value is determined for several temperatures from 1100° to 1800°K , data for which are given in Table IV.

Heating of the film causes the removal of molecular

Table IV.

Temperature °K	Accommodation Coefficient 25°C	Accommodation Coefficient 100°C
1182	.1495	—
1192	—	.1490
1295	.1466	—
1316	—	.1460
1342	.1440	—
1458	.1540	—
1558	—	.1700
1572	.1677	—
1695	—	.1826
1700	.1732	—
1733	—	.1830

oxygen, a minimum value of the accommodation coefficient occurring at 1300°K. Above this temperature the value rises, a maximum being apparent at 1700°K. At higher temperatures atomic oxygen is removed from the tungsten surface.

Below 1340°K there is a gradual drift in the value of the accommodation coefficient with time, due to the presence of oxygen in the system. At higher temperatures there is no drift

in the accommodation coefficient up to at least 8 minutes after heating. The increase in accommodation coefficient at these higher temperatures together with the disappearance of drift indicates a rearrangement of the film so that the surface becomes completely covered with atomic oxygen (16).

It is interesting to note that at 100°C , the maximum value of the accommodation coefficient obtained at 1700°K is the same as the value at the minimum (0.183) in an ordinary experiment.

In order to investigate the problem of this minimum, a tungsten wire with a surface area smaller than the one used in the present determination is required. This is necessary so that the percentage of oxygen adsorbed by the wire in the initial part of a determination will be negligible in comparison to that going to the charcoal surface. However, as the end loss of such a wire at 100°C would be large in comparison to the heat loss to the gas, it appears impractical at present to attempt such measurements.

Suggestions.

In order to determine the heat of adsorption of the second film of oxygen on tungsten two isotherms were necessary. Since one had already been obtained at 25°C it was thought advisable to determine the other at 100°C . This was chosen so

that the temperature difference $T_2 - T_1$ in the Clausius Clapeyron equation (page 7) would be as large as possible, increasing the accuracy.

It is apparent from the results that this bath temperature neither gives optimum experimental conditions nor results. Due to a possible rearrangement at 100°C , giving an underlying surface different to that at 25°C , the calculations of the heat of adsorption from the isotherms are somewhat in doubt. In addition, the extrapolation of the 100°C a_f 's to zero pressure cannot be accurately done due to the time taken to reach a final value of the accommodation coefficient at low pressures.

As the pressure in the reservoir B decreases at a rate of about 5% per hour it was inadvisable to make determinations beyond 120 minutes. Incorporation of a second $2\frac{1}{2}$ litre reservoir in the oxygen system would double the capacity as well as the time to which determinations could be made.

Considering the above difficulties and the resulting questionability introduced into the data, it would be advisable at some future date to redetermine the isotherms at lower temperatures, say 0°C and 35°C . At such temperatures the end losses are small enough to allow the use of a short, fine wire, the resistance of which preferably would be about 15 ohms. In such

a determination, many of the difficulties encountered in the present experiments could be eliminated, the result being greater accuracy of measurement.

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